

ION TRANSPORT STUDIES OF A NEW HOT-PRESSED SODIUM ION CONDUCTING
SOLID POLYMER ELECTROLYTES: (1-X) PEO:XNAF**Lumeshwari Sahu**Department of Physics
Bharti Vishwavidyalaya, Durg –
491 001, Chhattisgarh, India**Archana Chandra**Government M.M.R. Post
Graduate College, Champa –
495 671, Chhattisgarh, India**Shubhika Angesh Chandra**Government Naveen College,
Saragaon, Janjgir Champa - 495
686, Chhattisgarh, India**ABSTRACT**

Ion transport studies of an new sodium ion conducting polyethylene oxide (PEO) based solid polymer electrolytes (SPEs): (1-x) PEO:xNaF where $0 \leq x \leq 50$ wt.%, are reported. The present SPEs films have been synthesized by recently prepared by hot-press method. The highest ionic conductivity ($\sigma \sim 4.3 \times 10^{-7}$ S.cm⁻¹) have been observed at 30 wt.% of NaF i.e. the composition: (70PEO:30NaF). This highest conducting composition is known as optimum conducting composition (OCC). Materials characterization have been studied with the help scanning electron microscope (SEM) and thermo-gravimetric analysis (TGA). Measurements of the ionic transference number (t_{ion}) have been made at room temperature to help understand the structure of the system's ionic nature. Activation energy (E_a) have been computed from the temperature dependent ionic conductivity studies.

Keywords- Solid polymer electrolytes, SEM, TGA, activation energy, ionic transference number

INTRODUCTION

Ion conducting solid polymer electrolyte (SPE) materials have been attracting widespread attention in recent times due to their technological potentials to fabricate thin film flexible/laminated all-solid-state electrochemical power sources viz. batteries, fuel cells, sensors, supercapacitors etc. (Gray, 1991; Chandra, 1981; Lasker & Chandra, 1989). The technological relevance of these materials was recognized only after the discovery of first solid polymeric electrolyte in 1973, followed by the demonstration of first practical thin film battery based on poly (ethylene oxide) PEO- Li⁺ - salt complex in 1979 (Fenton et al., 1973; Armand et al., 1979). Since then, a large number of polymer electrolyte materials involving variety of mobile ions viz. H⁺, Li⁺, Ag⁺, K⁺, Na⁺ etc., as principal charge carriers, has been discovered in the last nearly three decades (Agrawal & Pandey, 2008; Chandra, 2010; Chandra et al., 2020, 2022;). Polymer

electrolyte films are formed, in general, via solution-cast route. However, recently, an alternate hot-press technique has been developed for casting completely dry polymer electrolyte films. Hot-press technique shows several procedural advantages over the traditional solution-cast method (Appetecchi et al., 2003; Agrawal & Pandey, 2008; Chandra et al., 2022). Recently, a new Na⁺ ion conducting SPEs: (1-x) PEO: x NaF, where $0 \leq x \leq 50$ wt.%, have been prepared by hot-press technique in our previous communication (Sahu et al., 2023).

In the present investigation, authors report the ion transport property studies of a newly synthesized PEO based hot-pressed Na⁺-ion conducting SPE films: (1-x) PEO: x NaF, where $0 \leq x \leq 50$ wt.% with the objectives to use them as electrolyte in the fabrication of all-solid-state polymeric film batteries. The materials characterization and polymer salt complexation have been explained with the help of SEM and TGA techniques. Ion transport behavior has been reported in terms of some basic ionic parameters viz. ionic conductivity (σ), ionic mobility (μ), mobile ion concentration (n), activation energy (E_a), ionic transference number (t_{ion}) measurements at various temperatures using the different experimental techniques.

EXPERIMENTAL

Dry powder of AR grade chemicals: polyethylene oxide (PEO) (10⁵ MW, Aldrich, USA), NaF (purity > 98%, Merck, India) have been used for the synthesis of newly SPEs: (1-x) PEO: x NaF, where $0 \leq x \leq 50$ wt.%. The detail related to synthesis of SPE films by hot-press method has been discussed in detail in our previous communication (Sahu et al., 2023). XRD patterns were recorded using Shimadzu X-ray diffractometer at Cu-K α radiation for the materials characterization/ polymer-salt complexation. SEM (model: JEOL, JXA-8100, Japan) has been used to study the surface morphology only on the hot-pressed SPE OCC film. The structural and thermal studies were done with the help of FTIR (model: Shimadzu-8400) and DSC (model: Perkin Elmer) techniques. The ionic conductivity measurements were carried out at room temperature using a LCR bridge (model: HIOKI 3520, Japan). The ionic mobility (μ) and ionic transference number (t_{ion}) measurements were also carried out at room temperature on the SPEs using the Transient Ionic Current (TIC) d.c. polarization technique (Watanabe et al., 1985; Chandra et al., 1988). Subsequently, the mobile ion concentration (n) values were evaluated from σ and μ data.

RESULTS AND DISCUSSION

Fig.1. shows the salt concentration-dependent conductivity variation at room temperature for the hot-pressed SPEs: $(1-x)$ PEO: x NaF, where $0 \leq x \leq 50$ wt.%. (Sahu et al., 2023). The SPE film composition: (70PEO:30NaF) with ionic conductivity of 4.3×10^{-7} S.cm⁻¹ at ambient temperature, have been identified as optimum ionic conducting composition (OCC) and conductivity enhancement have been explained.

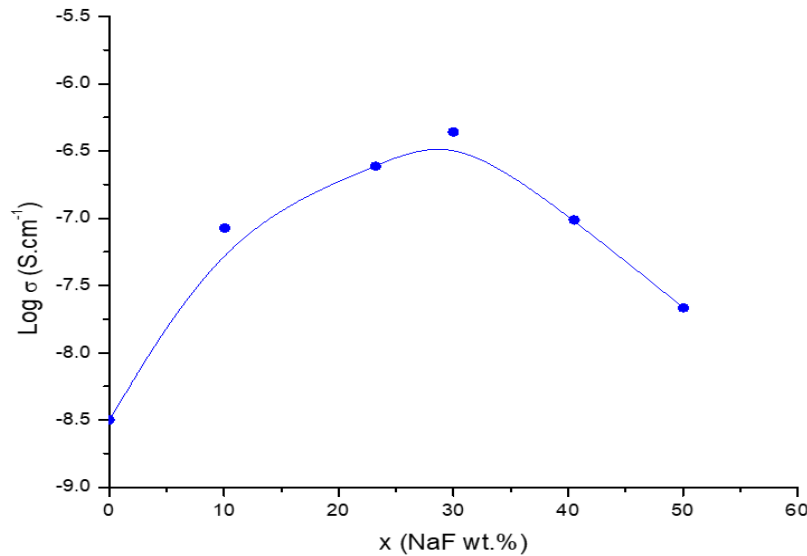


Fig.1: ‘Log σ -x’ plot for hot-pressed SPEs: $(1-x)$ PEO: x NaF, where $0 \leq x \leq 50$ wt.%. (Sahu et al., 2023)

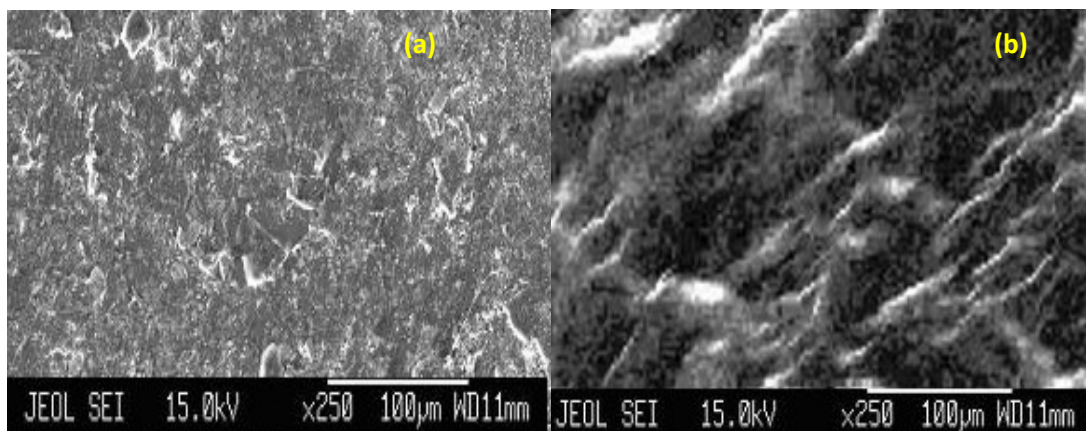


Fig.2: SEM images: (a) SPE OCC: (70PEO:30NaF) and (b) pure PEO.

Materials characterization have been done by the SEM and TG analysis, as mentioned in Experimental section. Fig. 2 shows the surface morphology of pure PEO and hot-pressed SPE OCC: (70PEO:30NaF). It is clearly indicated that the almost smooth surface morphology obtained in SPE OCC as compared to pure PEO. It is also closely related to the reduction of degree of crystallinity and enhancement of amorphicity as with NaF salt, while pure PEO usually shows a rough morphology (Chu et al., 2003).

Figure 3 shows the thermo-gravimetric analysis (TGA) curves for pure PEO, SPE OCC: (70PEO:30NaF). It can be clearly observed from the figure that the total weight loss for pure PEO is larger as compared to the newly synthesized SPE OCC. The total weight loss for SPE OCC is ~ 77 % whereas for pure PEO is ~ 95 %. The thermal stability of polymer is improved when the complexation with NaF and this is also great evidence for the conductivity enhancement. Similar type of behavior has also been reported in literature (Chandra, 2017;Chandra et al. 2022).

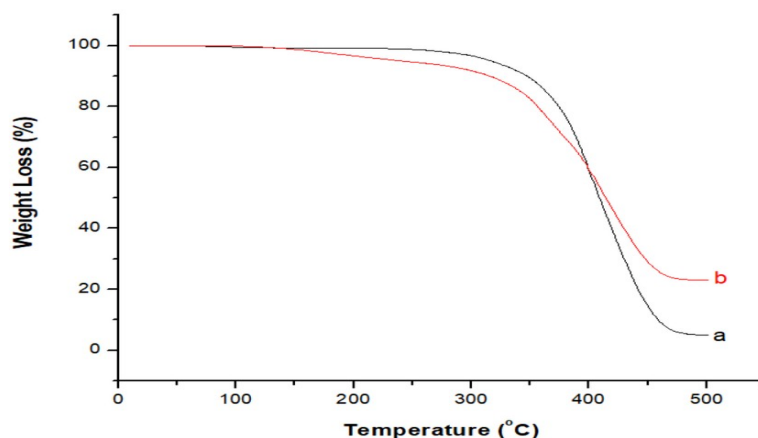


Fig. 3: TGA curves: (a) pure PEO and (b) SPE OCC: (70PEO:30NaF).

The ionic transference number (t_{ion}) for SPE OCC was evaluated at room temperature using dc polarization technique, as mentioned in experimental section. $t_{ion} \sim 0.95$, indicates the fact that the ions are the principal charge carriers in SPE film material. However, the main transporting ionic species are yet to be identified, as both cations as well as anion usually move in the polymer electrolyte system. Since, Na^+ ions, are much smaller in size than F^- ions, hence, it may be thought that Na^+ ions are probably the principal charge carriers in this system.

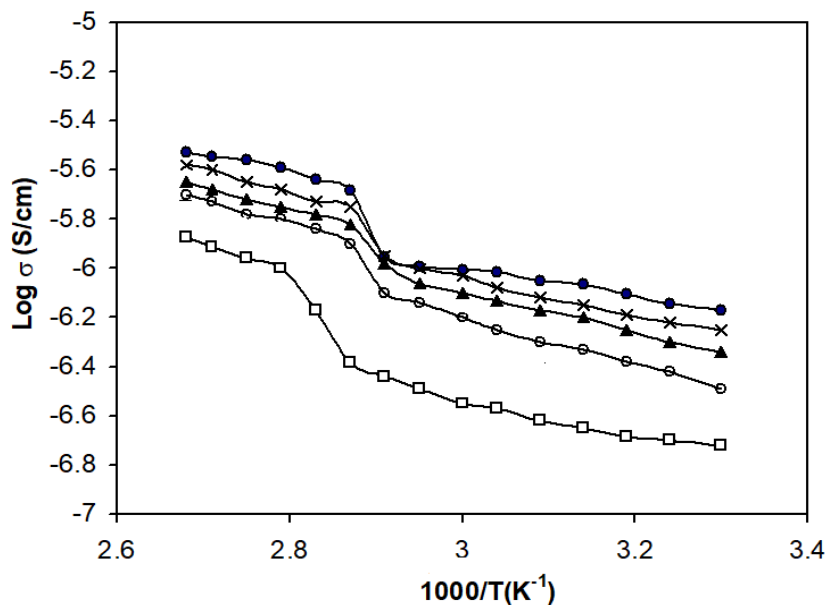


Fig. 4: ‘Log σ -x’ plots for SPEs: (1-x) PEO: xNaF, where x = 10 (□), 20 (▲), 30 (●), 40 (×), 50 (○).

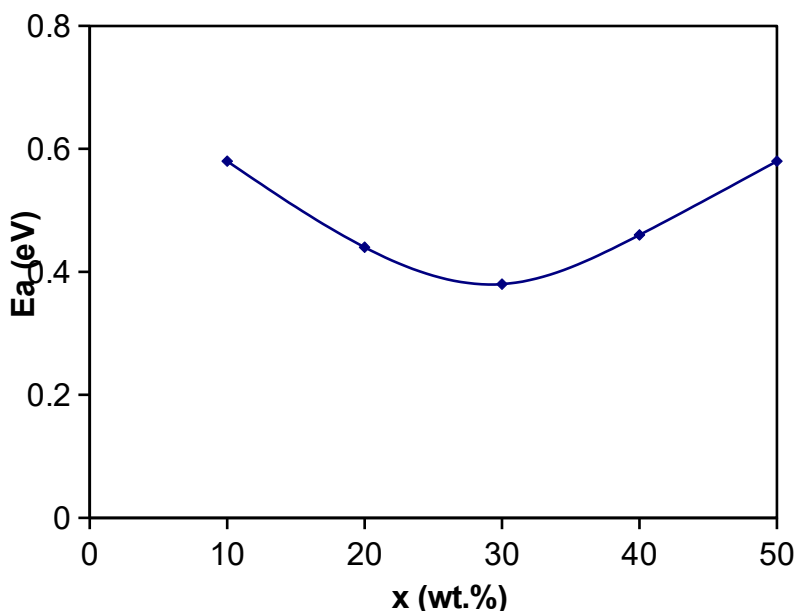


Fig.5: ‘Activation energy (E_a) vs x’ plot for SPEs: (1-x)PEO:xNaF.

To evaluate the activation energy (E_a) values, encountered by the transporting ions within the bulk, the temperature dependent conductivity measurements have been carried out on hot-pressed SPE films: (1-x) PEO: x NaF. Fig. 4 shows ‘log σ - 1/T’ plot for the SPEs. The conductivity increased almost linearly with temperature up to ~ 70 °C at which an upward jump

in conductivity was observed followed again by the gradual increase in conductivity in all the compositions. The jump in σ at this temperature correspondsto semi-crystalline to amorphous phase transition temperature (T_m) of PEO. The linear portion of ‘ $\log \sigma -1/T$ ’ plots below T_m can be expressed by following Arrhenius equation:

$$\log \sigma = \log \sigma_o \exp (- E_a/ kT) \quad [\text{Scm}^{-1}]$$

where E_a is the activation energy (in eV), involved in the thermally activated process. The E_a values, for all the compositions, were computed from linear least square fitting of the above equation and plotted as a function of x , as shown in Fig. 5. It can be clearly noticed that for OCC SPE film, the activation energy $E_a \simeq 0.38$ eV is lowest as compared to other SPE films. Low ‘ E_a ’ is indicative of relatively easier ion migration in the hot-pressed solid polymer electrolyte film and this can be potentially used as electrolyte to fabricate all-solid-state polymer batteries.

CONCLUSIONS

Ion conduction mechanism of newly synthesized solid polymer electrolytes (SPEs): (1-x) PEO: x NaF, wt.% have been successfully explained with the help of various experimental and theoretical models. The polymer-salt complexations have been confirmed by SEM and TGA studies. Ionic transference number (t_{ion}) ~ 0.95 obtained and it is indicted that SPE is predominantly anion conducting material with Na^+ -ion be the principal charge carriers. Lower activation energy in SPE OCC indicated that this can be employed as electrolyte to fabricate all-solid-state polymeric film batteries.

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